

# Hydrophobic, mechanical, and tribological properties of fluorine incorporated hydrogenated fullerene-like carbon films

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**Abstract:** Fluorine-incorporated hydrogenated fullerene-like nanostructure amorphous carbon films (F-FLC) were synthesized by employing the direct current plasma enhanced chemical vapor deposition (dc-PECVD) technique using a mixture of methane ( $\text{CH}_4$ ), tetra-fluoromethane ( $\text{CF}_4$ ), and hydrogen ( $\text{H}_2$ ) as the working gases. The effect of the fluorine content on the bonding structure, surface roughness, hydrophobic, mechanical, and tribological properties of the films was systematically investigated using Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Raman analysis, atomic force microscope (AFM), contact angle goniometer, nano-indenter, and reciprocating ball-on-disc tester, respectively. The fluorine content in the films increased from 0 to 2.1 at.% as the  $\text{CF}_4$  gas flow ratio increased from 0 to 3 sccm, and incorporated fluorine atoms existed in the form of  $\text{C}-\text{F}_X$  ( $X = 1, 2, 3$ ) bonds in the film. The fullerene nanostructure embedded in the hydrogenated amorphous carbon films was confirmed by Raman analysis. The water contact angle was significantly increased because of fluorine doping, which indicates that the hydrophobicity of the carbon films could be adjusted to some extent by the fluorine doping. The hardness and elastic modulus of the films remained relatively high (22 GPa) as the fluorine content increased. Furthermore, the friction coefficient of the carbon films was significantly reduced and the wear resistance was enhanced by fluorine doping.

**Keywords:** fullerene-like carbon film; fluorine doping; hydrophobicity; mechanical properties; tribological performance

## 1 Introduction

Hydrogenated diamond-like carbon (DLC) films have attracted significant interest in the area of science because of their extraordinary properties such as high mechanical hardness, low friction coefficient, and high wear resistance [1–4]. These properties make them excellent candidates for a wide range of applications. Generally, the mechanical properties are mainly determined by the  $\text{sp}^3$  hybrid carbon content, which contributes to higher mechanical hardness. It should be noted that our previous studies have reported films with a hardness of 20.9 GPa and elastic recovery as high as 84%, and these excellent properties were

attributed to the unique fullerene-like nanostructure embedded in the amorphous diamond-like carbon matrix [5, 6]. However, fullerene-like nanostructure carbon (FLC) films with high  $\text{sp}^2$  hybrid carbon content showed excellent mechanical properties. This is due mainly to the presence of the curvature in an all- $\text{sp}^2$  three-dimensional network, as with a “molecule spring” fixed in the amorphous carbon matrix [7, 8]. This also indicates that the  $\text{sp}^3$  hybrid carbon content is not the only factor that determines the mechanical properties of the film, as the microstructure also significantly affects the mechanical properties.

From the above discussion, fullerene-like nanostructure carbon films have promising and valuable prospect as protective coating. Furthermore, it is well known that the incorporation of non-metallic elements, including N [9], Si [10, 11], and F [12–14], can

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significantly improve and modify the performances of films. Among them, fluorine incorporated DLC films have attracted significant interest due to their superior low friction coefficient, low surface energy, low internal stress, particularly excellent biocompatibility, and hydrophobic properties. Yu et al. [15] found that the F content rapidly increased with the introduction of  $\text{CF}_4$ , leading to a sharp reduction in the surface energy of the film. Marciano [16] also reported that F-DLC films presented lower stress and surface free energy as their F content increased. In addition, according to Refs. [17, 18], the biocompatibility and hydrophobic properties can be effectively improved by the incorporation of fluorine. Recently, a number of deposition technologies have been proposed for the synthesis of F-FLC films [19–21]; the common deposition technique involves the use of a pulsed direct current plasma enhanced chemical vapor deposition (dc-PECVD) system, which has several advantages such as low film stress, low deposition temperature, and good uniformity on a large-area substrate.

Considering the complexity and diversity of amorphous carbon film, in our present work, we synthesized fluorine-incorporated hydrogenated fullerene-like amorphous carbon films (F-FLC) by employing the pulsed dc-PECVD technique using a mixture of methane ( $\text{CH}_4$ ), tetra- fluoromethane ( $\text{CF}_4$ ), and hydrogen ( $\text{H}_2$ ) gases. The aim of this work is to study the effect of the F content on the properties of FLC film, and to determine whether the hydrophobic, mechanical, and tribological properties of the FLC film can be significantly improved by fluorine doping.

## 2 Experimental details

### 2.1 Film deposition

All of the films were prepared on a Si substrate (n-100) using the dc-PECVD technique. The substrate was sequentially ultrasonic cleaned in ethanol and acetone for 10 min to remove surface stains, then dried in the ambient atmosphere and placed into the chamber. Prior to the deposition, the vacuum chamber was evacuated up to  $1.0 \times 10^{-3}$  Pa, and then 300 sccm argon was introduced into the chamber. The entire Si substrate was first cleaned by argon discharge for 30

min at a discharge voltage of  $-800$  V. During this time, the working pressure was kept at 4.8 Pa. The working gas of the deposition was composed of 300 sccm Ar, 10 sccm  $\text{CH}_4$ , and 20 sccm  $\text{H}_2$ . The diameters of the upper electrode and the substrate holder were 300 and 200 mm, respectively, and the distance between the two electrodes was 5 cm. A negative pulsed voltage of 1,000 V and a duty-cycle of 80% were applied to the substrate, and the working pressure was kept at 15 Pa. The deposition time was set as 120 min. The fluorine content was controlled by varying the  $\text{CF}_4$  gas flow to 0, 1 sccm, 1.5 sccm, and 3 sccm. The substrate is not heated, while the temperature was unintentionally increased to around  $100^\circ\text{C}$  because of the plasma bombardment during the deposition process. After processing, the samples were cooled down inside the chamber.

### 2.2 Sample characterization

The thickness of the films was measured using cross-section scanning electron microscope (SEM) images, and the deposition rate can be obtained by the ratio of the thickness to the deposition time. The bonding structure and the chemical state were characterized using Fourier Transform Infrared Spectroscopy (FTIR) in the range of  $400\text{--}4,000\text{ cm}^{-1}$ , with a  $2\text{ cm}^{-1}$  resolution and 32 scan times at room temperature. The microstructure of the films was characterized by VG ESCALAB 210 type X-ray photoelectron spectroscopy (XPS), with Al  $\text{K}\alpha$  radiation (photo energy  $1476.6\text{ eV}$ ) as the excitation source and using a Raman spectrometer (Jobin Yvon T64000) in back-scattering configuration with laser excitation at a wavelength of  $514.5\text{ nm}$ , which is over the  $800\text{--}2,000\text{ cm}^{-1}$  wavenumber range. The surface topography was observed by a Smart SPM type atomic force microscope (AFM, AIST-NT Co, USA), and the relative roughness factor (Ra) was calculated by the analysis of a Nanoscope III 5.12r2 program. The hydrophobicity examination of the film was performed using purified water by employing the sessile drop method with a DSA100-type (KRUSS Co., Germany) contact angle goniometer, which has an accuracy of  $2^\circ$ . For each sample, 5 different surface location measurements were evaluated to obtain average values, and all measurements were reported as the mean of 5 replicates to obtain more

reliable data. The hardness and elastic recovery were measured by a nanoindenter (Nano indenter II, MTS. Co., USA) with a maximum indentation depth of 50 nm. The tribological properties were tested using a UMT-2MT ball-on-plate reciprocating tribo-tester, which slides at 25°C and at a relative humidity (RH) of 15%–19%. As the mating material,  $\text{Al}_2\text{O}_3$  balls ( $\phi 5$  mm) were ultrasonic cleaned with acetone before each test. All of the measurements were performed at a sliding velocity of 15 cm/s and with a 30 N load. The sliding distance was 90 m. The specific friction coefficient was calculated by averaging the data of at least 5 individual operations. After friction, the wear morphologies of mating balls and scars of the films were observed by SEM. The wear volume was calculated by measuring the wear scars of the substrate with a three-dimensional profilometer, and then the specific wear rates ( $k$ ) of the films were obtained from Eq. (1) as follows

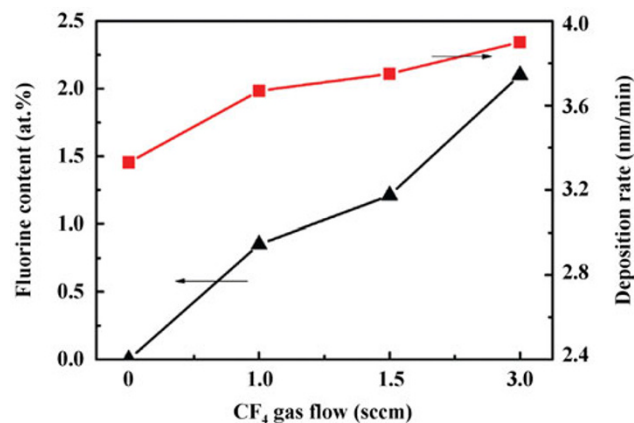
$$k = V / (D \cdot L) \quad (1)$$

where  $V$  is the wear volume of the samples,  $D$  is the sliding distance, and  $L$  is the sliding load.

### 3 Results and discussion

#### 3.1 Fluorine content, deposition rate, and fluorine atoms bond state

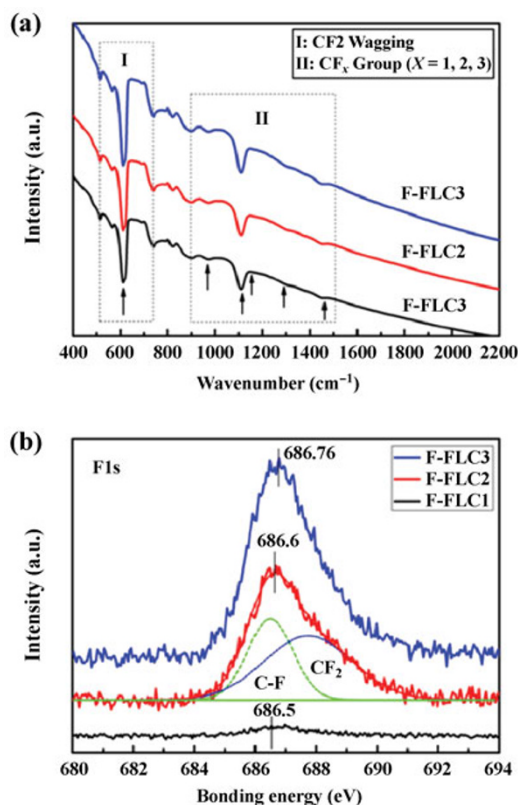
Figure 1 depicts the dependence of the fluorine content and deposition rate of the films on the  $\text{CF}_4$  gas flow. It is clear that the fluorine content increases with the increase of the  $\text{CF}_4$  gas flow (confirmed by XPS). As



**Fig. 1** The dependence of the fluorine content and the deposition rate on the  $\text{CF}_4$  gas flow.

the  $\text{CF}_4$  gas flow increases from 0 to 1 sccm, the fluorine content increases from 0 (FLC) to 0.85 at.% (F-FLC1). As the  $\text{CF}_4$  gas flow increases further, the fluorine content increases from 1.21 at.% (F-FLC2) to 2.1 at.% (F-FLC3). The result implies that the fluorine content can be adjusted by varying the  $\text{CF}_4$  gas flow, which is consistent with the results of many studies [22–24]. Furthermore, the deposition rate of the films still increased slightly from 3.3 nm/min to 3.9 nm/min as the  $\text{CF}_4$  gas flow increased from 0 to 3 sccm.

Figure 2(a) shows the FTIR spectrum of the films. The C–F vibrational modes for the wavenumber range of 400–2,200  $\text{cm}^{-1}$  are listed in Table 1 [25, 26]. The broad peak at 2,950  $\text{cm}^{-1}$  for the  $\text{CH}_n$  group and the bond at 1,600  $\text{cm}^{-1}$  of C=C stretching are so weak that it is not easily found. This indicates that there is little hydrogen in the films. Besides, the FTIR spectrum can be divided into two groups: the absorption peak located at 600  $\text{cm}^{-1}$ , which is associated with the  $\text{CF}_2$  wagging mode (Group I), and a broad band observed in the range of 980–1,500  $\text{cm}^{-1}$  (Group II). The peak



**Fig. 2** (a) the FTIR spectrum and (b) the XPS F1s peak of the film as a function of the fluorine content.

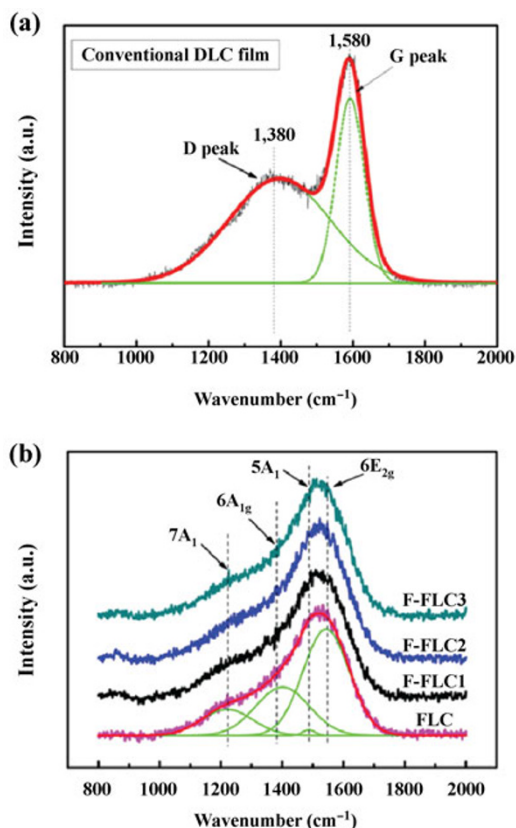
**Table 1** FTIR assignment for different vibrational modes of F-DLC films.

Group	Wavenumber (cm <sup>-1</sup> )	Vibrational modes
I	650	CF <sub>2</sub> wagging
II	980	CF <sub>3</sub>
	1030	CF
	1050	CF in CF <sub>2</sub>
	1160	CF <sub>2</sub> symmetric stretch
	1220	CF <sub>2</sub> asymmetric stretch
	1340	CF stretch
	1450	CF <sub>2</sub> asymmetric stretching

near 1,000 cm<sup>-1</sup> is attributed to the C–F bond and the sharp peak at 1,100 cm<sup>-1</sup> is due to CF<sub>2</sub>. Moreover, the XPS F 1s spectra of the films with different fluorine contents are shown in Fig. 2(b). The intensity of the F 1s peak clearly increased and the peak position shifted slightly toward a higher binding energy with an increase in the fluorine content from 686.5 eV for the F-FLC1 film to 686.6 and 686.8 eV for the F-FLC2 and F-FLC3 films, respectively. The F1s spectra could be divided by the Gaussian fitting into two peaks, centered at 686.4 eV and 687.8 eV, related to the C–F and C–F<sub>2</sub> bonding, respectively. The higher F content in the film clearly leads to a higher C–F<sub>2</sub> content, resulting in a higher binding energy shift. The results from the FTIR and XPS F1s analysis suggested that the incorporated fluorine atoms exist mainly in the form of the C–F, C–F<sub>2</sub>, and C–F<sub>3</sub> bonds in the film.

### 3.2 Raman analysis

Raman spectroscopy, which is a popular, effective, and non-destructive tool that is used to distinguish different bonding types, was used to probe the bonding structure of the carbon films. Figure 3 displays the Raman spectra of the conventional amorphous carbon film and the FLC films. A broad asymmetric Raman band, which represents the typical features of the conventional DLC films, could be observed in the wavenumber range of 800–2,000 cm<sup>-1</sup> (Fig. 3(a)). Normally, the Raman spectrum can be fitted into two Gaussian peaks: (1) a relatively sharp peak (so-called G peak), which originated from all pairs of sp<sup>2</sup>-C atoms in both rings and chains, is located at about 1,580 cm<sup>-1</sup>, and (2) a shoulder peak (D bond), which is assigned to the breathing mode of sp<sup>2</sup>-C atoms

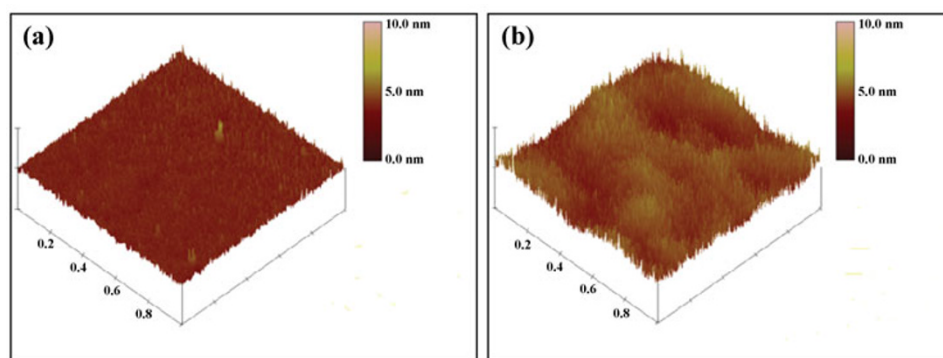
**Fig. 3** The Raman spectra of (a) the convention DLC film and (b) the FLC films.

only in aromatic rings, appeared at approximately 1,380 cm<sup>-1</sup> [27]. However, in addition to the D and G peaks, two additional Gaussian peaks centered at approximately 1,230 cm<sup>-1</sup> and 1,490 cm<sup>-1</sup> were also observed, as shown in Fig. 3(b), which is consistent with our previous results [5, 28] that indicated that these two peaks originated from the seven- and five-number carbon rings of curved graphite, fullerene, or onion.

### 3.3 Surface roughness and hydrophobicity

The relative roughness factor (Ra) roughness of the film surface was obtained using the smart SPM-type AFM technique, as shown in Fig. 4. Table 2 summarizes the specific Ra values as a function of the fluorine content. For a fluorine content of 0, the film has a flat and smooth surface and the Ra value is 0.37 nm. When the fluorine content increased up to 2.1 at.%, the surface of the film becomes rougher and many protuberances appear, and the Ra value also increases significantly from 0.37 nm to 1.07 nm. The effects of the





**Fig. 4** AFM images of the film with a fluorine content of (a) 0 and (b) 2.1 at.%.

**Table 2** The surface roughness (Ra) of the films as a function of the fluorine content.

Samples	Ra roughness (nm)
FLC	0.37
F-FLC (F = 0.85 at.%)	0.59
F-FLC (F = 1.21 at.%)	0.72
F-FLC (F = 2.10 at.%)	1.07

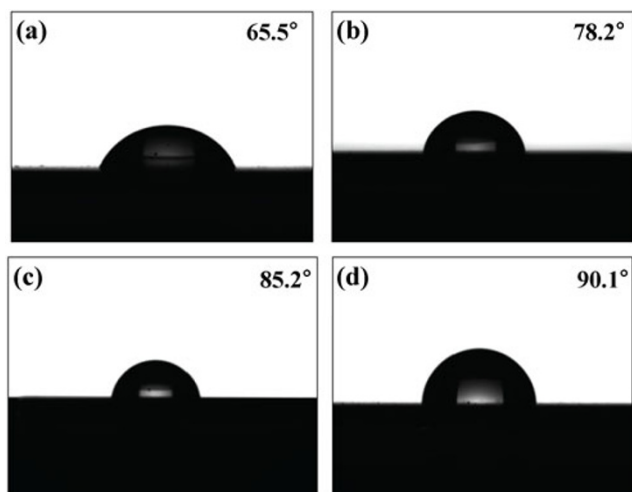
ions' bombardment may contribute to the increased surface roughness [29]. With the increase of the fluorine content, an increasing number of  $F^+$  ions bombarded the film surface, which would promote increased surface roughness.

The hydrophobicity of the films was determined by the water contact angle. Figure 5 shows the variation of the water contact angles as a function of the fluorine content. Clearly, the water contact angle continuously increases with the fluorine content. The water contact

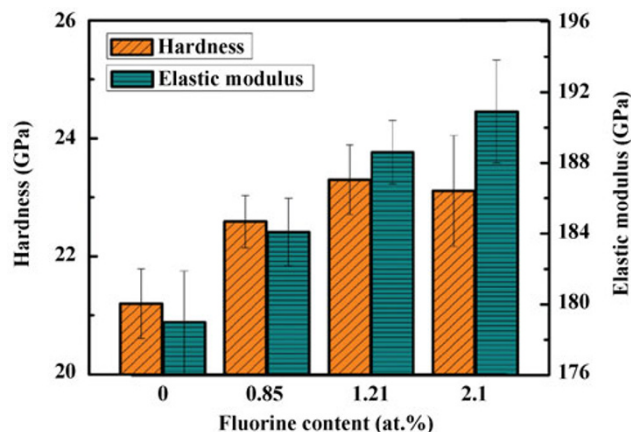
angle is  $65.5^\circ$  for the FLC film, and quickly increases to  $78.2^\circ$  for the F-FLC1 film. Eventually, the water contact angle reaches  $90.1^\circ$  for the F-FLC3 film. This suggests that the increase in the water contact angle is due mainly to the incorporation of F, which is consistent with Ref. [30]. It is clear that the increase in the water contact angle is due not only to the presence of  $CF_x$  bonds, but also to the surface roughness. Previous studies [31, 32] have shown that the surface roughness can significantly affect the hydrophobicity of the films, as a smoother surface will result in a smaller water contact angle. As the fluorine content increases, the surface roughness increases, as shown in Table 2, leading to the increased water contact angle.

### 3.4 Mechanical and tribological properties

Figure 6 illustrates the hardness and elastic modulus of the films as a function of the fluorine content. The lowest hardness of about 21.2 GPa and elastic modulus of around 179 GPa were observed for the FLC film. As the fluorine content increases, the hardness and elastic modulus increase to 22.6 GPa and 184.1 GPa for the F-FLC1 film, respectively. Ultimately, for the F-FLC3 film, the hardness and elastic modulus increase to 23.1 GPa and 191 GPa, respectively. Generally, the hardness and elastic modulus of the film will decrease due to the fluorine doping, which, because it is a termination radical, could disrupt the continuity of the C–C network [33]. However, in this study, the hardness and elastic modulus monotonously increase with the increasing fluorine content. The bombardment effect of the  $F^+$  ions should be considered because the  $F^+$  ions bombardment results in not only an increase in the film density, but also the increase of compressive



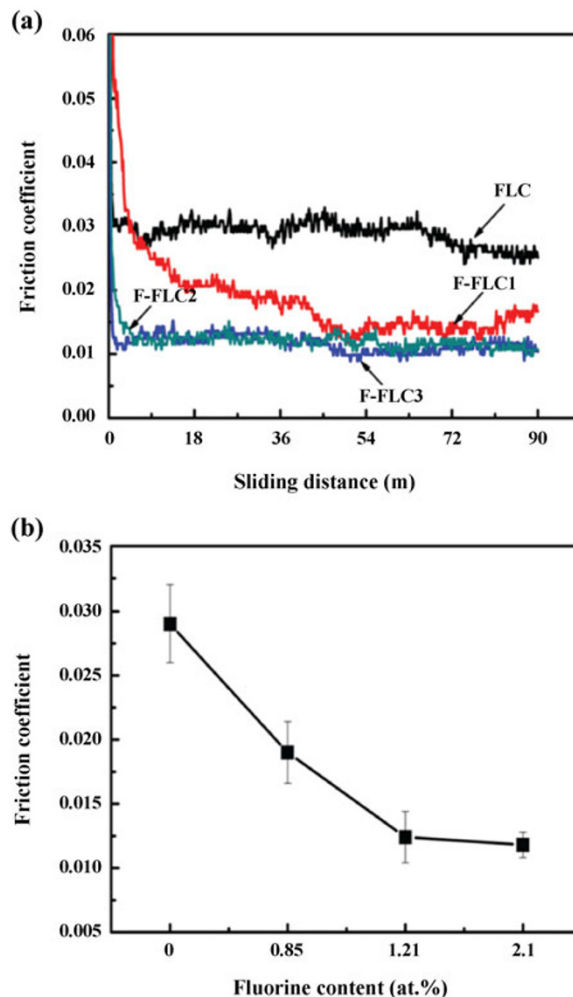
**Fig. 5** Water contact angles for the film with a fluorine content of (a) 0, (b) 0.85 at.%, (c) 1.21 at.%, and (d) 2.1 at.%.



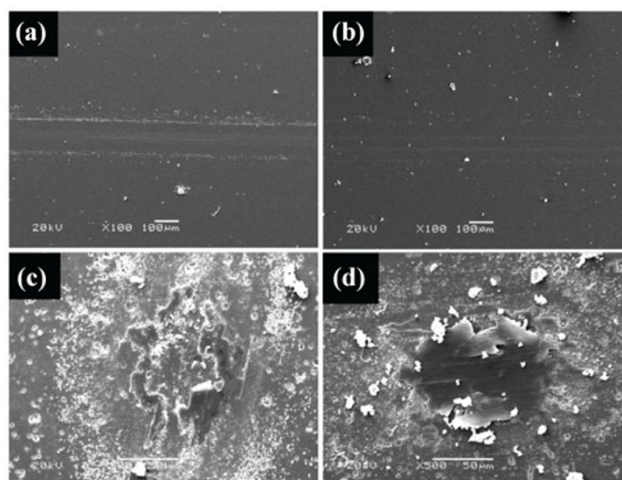
**Fig. 6** The elastic modulus and hardness of the F-FLC films as a function of the fluorine content.

stress in the film. The increased hardness and elastic modulus may be due to a combination of the increases in both the density and the compressive stress.

The friction and wear property of the films were measured on the reciprocating ball-on-disc tester. The friction coefficient curves of the films as a function of the fluorine content are shown in Fig. 7(a), and the steady state friction coefficients are also given in Fig. 7(b). It can be observed that the FLC film presents a high friction coefficient of around 0.029. When the fluorine content increases to 0.85 at.%, the friction coefficient sharply decreases to 0.019. When the fluorine content then increases to 2.1 at.%, the lowest friction coefficient of about 0.011 was obtained. Figure 8 shows the wear surface and the corresponding wear scar of the matching ball. There is some obvious wear debris scattered on both sides of the wear track for the FLC film, while no obvious wear was found, as shown in Fig. 8(b). Moreover, the corresponding wear scar of the matching ball for the FLC film is also obviously larger than that of the F-FLC3 film (2.1 at.%), which implies that the F-FLC film possesses more excellent wear resistance compared with the FLC film. The specific wear rate of the F-FLC3 film is  $5.3 \times 10^{-9} \text{ mm}^3/\text{Nm}$ , much lower than that of the FLC film, which is around  $15 \times 10^{-9} \text{ mm}^3/\text{Nm}$ . There is usually a close relationship between the tribological and mechanical properties, and the outstanding wear resistance of the F-FLC3 film may be attributed to its higher hardness and elastic modulus. This result indicates that a much better wear resistance could be obtained by fluorine doping.



**Fig. 7** Friction coefficient of the F-FLC films as a function of the fluorine content.



**Fig. 8** Wear surface of the films with the fluorine content of (a) 0 and (b) 2.1 at.% and the corresponding wear scar (c) and (d) of the contact balls.

## 4 Conclusions

Fluorine incorporated hydrogenated fullerene-like nanostructure carbon films were deposited on the Si wafer using the dc-PECVD technique. The fluorine content increased from 0 to 2.1 at.% as the  $\text{CF}_4$  gas flow increased from 0 to 3 sccm. The influence of the fluorine content on the bonding structure, hydrophobicity, and mechanical and tribological properties of the films were investigated systematically. Both the fluorine content and deposition rate increased with the increase of the  $\text{CF}_4$  gas flow. The FTIR and XPS analyses indicated that the incorporated fluorine atoms exist in the form of  $\text{C-F}_x$  ( $x = 1, 2, 3$ ). Raman spectroscopy showed that the fullerene nanostructure has been successfully embedded in the amorphous carbon film. The AFM images suggested that the surface roughness increased with the increase of the fluorine content, which may be due to the bombardment of the  $\text{F}^+$  ions. As a result, the hydrophobicity, which is assessed using the water contact angles, has been effectively improved. However, the hardness and elastic modulus were not reduced, but with an increase tendency although the degree of the increase is very small, which may be attributed to the slight increases in the film density and the compressive stress induced by the  $\text{F}^+$  ion bombardment. In addition, the lower friction coefficient and outstanding wear resistance could also be obtained by fluorine doping, which is mainly due to the excellent mechanical properties.

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